

SCIENCE FOR CERAMIC PRODUCTION

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SYNERGISTIC AND QUASICHEMICAL APPROACHES IN CERAMIC TECHNOLOGY (A REVIEW)

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The prospects of using the synergistic and quasichechemical approaches to various stages of ceramic technology, i.e., powder preparation, molding, and sintering are considered.

The current level of properties of ceramics and their stability is sufficient for many application areas. Some new application areas, for instance, machine building and electronics impose more severe requirements on the reproducibility of structure and properties from one sample to another. A key to solving this problem is supplied by synergism and chemistry of crystals with defects [1, 2].

The present paper does not consider mathematical apparatus developed for synergism. This apparatus is complicated enough and is currently being developed by professional mathematicians [3].

Our attention is focused on the principal unstable states and multistability (a variety of stable states) in a system, which have a determining effect on the evolution of the material structure at a particular stage of ceramic technology [4]. Affecting a system in the range of a main unstable state for the purpose of eliminating multistability is an efficient way for improving the reproducibility of a ceramic structure. If an unstable state is a bifurcation (according to I. R. Prigogine, a bifurcation is an unstable state, after which the course of evolution is unpredictable and the probabilistic aspect of matter is manifested), then, instead of elimination of multistability one sometimes uses the term of elimination of a bifurcation [5, 6].

A very significant factor in the formation of a ceramic structure consists in selection of additives acting as dopant impurities in a solid solution and selection of methods for their introduction, which are based on the quasichechemical approach (record of defect formation using reactions resembling chemical reactions) developed by P. V. Kovtunenkov [2]. It should be admitted that a formally correct record of a quasichechemical reaction (reaction of defect formation) does

not guarantee that its occurrence in reality. Similarly to normal chemical reactions, a proof can be obtained by studying the reaction products. Unfortunately, this is rather difficult to implement as yet for quasichechemical reactions, which is the main factor restricting the wide application of this approach. However, involvement of general chemical regularities gives substantial grounds for supposing the existence of probable quasichechemical reactions, and they can be used not only to interpret the phenomena observed, but also to find ways to improve ceramic technology.

According to concepts of synergism, the development of ceramic technology should start with identifying the main unstable states. The latter are responsible for insufficient reproducibility of ceramic articles. If an unstable state is a bifurcation, sometimes its preservation due to self-organization makes it possible to obtain a desired structure. At present we have only a general consideration that a certain degree of nonequilibrium ought to be provided for this purpose.

Normally reproducibility is improved by eliminating multistability. Internal (prehistory) or external controlling signals exceeding the noise level (slight uncontrolled inner fluctuations or outer disturbances) are used to influence a system in an unstable state. In the case of a bifurcation, noises act as controlling signals. Internal signals are elements of a ceramic structure (at sub, micro-, and macrolevel) developed at preceding technological stages. The role of external signals is played by various outside factors affecting the system: temperature, partial pressure of the gaseous medium components, flows of molecules, atoms, ions, electrons, photons, and other types of radiation, various fields (electromagnetic, mechanical, etc.). If the bifurcation persists or is eliminated by means of an external controlling signal, the “memory” of the preceding structure is lost. In this sense the choice of dopant impurities based on the quasichechemical approach and their introduction into a ceramic mixture repre-

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sent the use of internal signals to control the evolution of the system.

In order to ensure a prevalence of an internal or an external signal over noises, it is convenient to reduce the latter. Noise often expresses a reaction of a system to an external action and the degree of its nonequilibrium. Some authors believe that these are auto-waves generated within the system [7]. To decrease the noise level, the degree of nonequilibrium in the unstable state interval ought to be decreased. An increase in the degree of nonequilibrium in this interval, on the contrary, increases the amplitude of fluctuations (noises) in the system. An increased amplitude may transform them into controlling signals, which will ensure the formation of a desirable structure [8].

Let us consider the advantages of the synergistic and quasichemical approaches. Considering the effect of prehistory, technologists are convinced that the crucial role in technology is played by preparation of highly dispersed ceramic powders, which is the first stage in ceramic technology. However, such powders frequently enough produce coarse-crystalline ceramics with inter- and intra-crystal pores. The reason is that the condition providing for inheritance of the structure, i.e., a reliable excess of the internal controlling signal over noises is not complied with at subsequent technological stages.

Recently certain techniques have been developed yielding nearly monofractional powders consisting of spheroid particles sized 1 μm or less [9]. Subject to a certain sufficiently high degree of the process nonequilibrium, the system organizes itself into particles or aggregates of required shape and size. This has been implemented in preparing powders using chemical (particles and aggregates) and mechanical (granules) methods.

A high degree of nonequilibrium in producing ceramic powders forces the system to accumulate in itself a significant part of excessive energy for the formation of defects of various sizes, starting with point defects. Immediately after obtaining particles of size 1 μm and less, conditions should be developed facilitating the inheritance of the existent structure, to prevent the formation of coarse strong and compact aggregates. For this purpose, the degree of nonequilibrium of the process is reduced: water is replaced by an organic medium, material is rapidly frozen with subsequent removal of ice by sublimation, supercritical conditions for the dispersion medium are developed, or surfactants are applied.

An example of elimination of a bifurcation using an external controlling signal is the production of powders by ultrasonic spraying of solutions unto a hot furnace [10]. The ultrasonic sprayer creates drops of nearly equal sizes, after which conditions have to be created for inheriting this structure, first of all to prevent adhesion of drops by decreasing their concentration in the gaseous phase.

Highly dispersed monofractional powders can be obtained through self-organization of a system with a high degree of nonequilibrium. True, the theory cannot yet provide an answer regarding the conditions, under which this will

happen and whether it will happen at all. A promising way to increase reproducibility is to eliminate a bifurcation using an external controlling signal in the form of periodic energy fields, for instance, ultrasonic fields. By varying the parameters and types of these fields it is possible to produce highly dispersed, nearly monofractional powders with required particle sizes. In preparing ceramic powders it is most convenient to introduce doping impurities which act as internal controlling signals in sintering of ceramics.

In molding, one usually tries to obtain a maximally compact intermediate article with a uniform density. At the same time, the use of powders with substantial excessive energy leads to a high degree of nonequilibrium facilitating the self-organization of the system and its evolution to the formation of a strong skeleton with vacancies. The skeleton has a fractal nature and can be described in the context of the percolation theory [11].

Elimination of multistability by means of an internal controlling signal, for instance, a correct choice of a temporary technological binder (TTB) provides for the structure of the molded piece evolving into a more consolidated skeleton with uniform density. Powder granulation is a very efficient and widely used method. Granules act as dissipative structures (structures arising as a consequence of self-organization of the system and ensuring efficient energy dissipation) and facilitate a decrease in the inner energy of the system. Instead of forming its own dissipative structures of different shapes and sizes (local compactions), the system uses structures pre-made by a technologist. Regulation of size, shape, and strength of granules and the force of friction between the granules allows for production of a sufficiently consolidated skeleton of uniform density.

Effective external controlling signals include periodic mechanical-stress fields arising in vibromolding and ultrasonic treatment. It is clear from the synergistic approach that a specific vibration regime is needed for each shape and material of molded articles, which is regarded as one of the main reasons impeding wide application of this molding method. Synergism makes it possible to understand the reasons of a positive effect of ultrasonic treatment on a molding mixture at a low pressure at the initial stage of semidry molding [12]. An ultrasonic field at a low pressure develops a structure consisting of local compactions in molding powder, which is inherited during a subsequent pressure rise and provides for more uniform density in molded articles.

It is possible to name two approaches in ceramic technology regarding the production of strong molded articles of uniform density.

The first approach consists in removing multistability using internal controlling signals, primarily, selection of a TTB. It makes it possible to obtain high-quality molded pieces on standard machinery under standard molding conditions [13].

The second approach is based on ensuring very low friction between powder particles when filling a mold with the mixture, whereas inside the mold the friction sharply grows

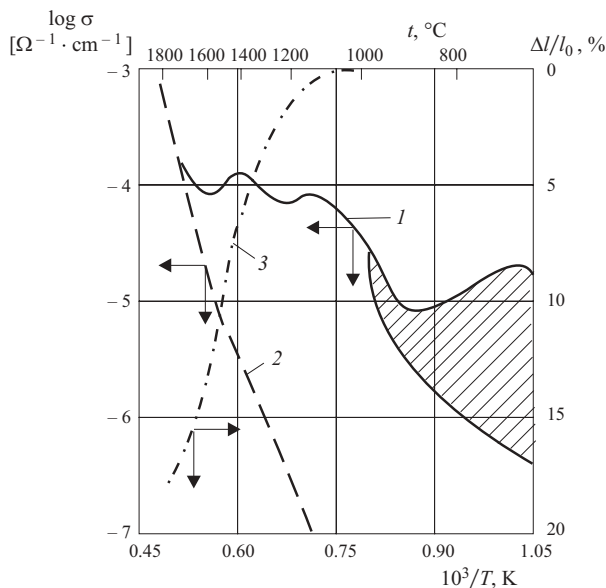


Fig. 1. Electric conductivity σ [heating (1), cooling (2)] and shrinkage $\Delta l/l_0$ (3) of molded corundum articles in sintering. The dashed segment indicates the interval of irreproducible values in the first heating of molded article.

providing for high strength of the molded piece. This occurs due to the modification of physicochemical properties of mixtures after filling the mold (in hot casting of paraffin slips). In principle, it is possible to achieve better results using this approach, however, it requires special equipment and molding regimes, which complicates its implementation. Furthermore, problems many arise at the subsequent stage of TTB removal. This line of research is highly promising, especially molding directly by casting aqueous slip into porous molds under pressure (injection molding), as well as using thermosetting technological binders. The problem is to provide for different flow properties of the mixture in filling the mold and after hardening inside the mold. At the same time, this approach opens possibilities for a finer control of shape formation and strengthening (curing) of a molded piece inside the mold.

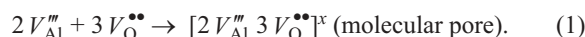
Similarly to the molding stage, local compactions may arise in removal of TTB and in the initial stage of sintering, which represents self-organization allowing for decreasing the surface energy by compaction of local sites of the molded article. It is convenient to study the evolution of local compactions by analyzing a surface fracture of the molded article [14]. With low strength of the molded article, the crack propagates mainly along the local compaction boundaries, and the size of the local compactions can be inferred from the fracture.

Firing dense oxide ceramics prepared from highly dispersed powders (solid-phase sintering without a chemical reaction) is accompanied passing via three the main unstable state intervals, which in our case are bifurcations [4].

The first main bifurcation in firing occurs at a temperature, when the fracture surface becomes smoother. It can be

registered employing a binocular magnifying glass in lateral illumination of the fracture surface [14]. If the bifurcation in this interval is preserved, the "memory" of preceding local compactions is lost, and new local compactions arise after the bifurcation. The uncontrolled formation of new local compactions during the bifurcation decreases the reproducibility of strength parameters, since the local compaction bounds in the case of their inheriting will act as stress concentrators and produce a significant spread in strength values. Local compactions constitute the precise reason for frequently found low strength and poor reproducibility of strength properties in ceramics obtained from highly dispersed powders. This interval approximately correlates with the first maximum, i.e., the first nonequilibrium phase transition (NPT) on the curve of electric conductivity of an article heated (Fig. 1) [15]. The first NPT is mainly related to perfecting the structure, when single vacancies formed as a consequence of impurity atoms, primarily hydroxyl groups being absorbed and dissolved in near-surface zones, reach the surface of the crystal. The process is accompanied by a decrease in the carrier concentrations and results in decreased conductivity. The size of the crystals does not grow, but the fractality of the crystal surface diminishes. Due to diffusion mass transfer in surface areas, the crystals acquire a more rounded shape. This facilitates relaxation of stresses, which are a consequence of local compactions arising in the molded article and can be a reason for smoothing of the fracture surface.

The vacancies reach the surface of the crystals and reduce friction between crystals, which later initiates shrinkage. As the degree of nonequilibrium in the first NPT interval increases (as the fractality of the surface decreases), an ever increasing part of energy is forced to accumulate in the near-surface layers in the form of vacancy associates, for instance, molecular and larger pores. In sintering of corundum this process can be written in the following form:



In sintering with a controlled rate of shrinkage, an exposure is organized in this temperature range, and temperature is even slightly lowered. In burning out TTB, molded articles are also heated to an approximately the same temperature. It makes sense to use external controlling signals to eliminate this bifurcation, for instance, ultrasonic fields, acoustic vibrations, etc.

The second main bifurcation in oxide sintering is observed under the maximum rate of sample shrinkage (an inflection on the shrinkage curve, a maximum on the differential shrinkage curve). This bifurcation presumably correlates with the second maximum in Fig. 1 (the second NPT) on the conductivity curve of an article heated. The plastic deformation of the skeleton controlled by mass transfer caused by volumetric diffusion produces a modification in the structure of the article molded.

Similarly to the first NPT, the process is limited by the volumetric diffusion of vacancies, which is corroborated by

the tangent of the relationship $\log \Delta l/l_0 - \log \tau$ ($\Delta l/l_0$ is shrinkage; τ is the duration of isothermic exposure) equal to 0.5 (Fig. 2) [15]. Sources of monovacancies are various nonequilibrium structural defects (substructure) and the outlet for vacancies is the material at the crystal boundary. The arrival of vacancies to the surface layer diminishes friction between the crystals. In this case the surface tension becomes sufficient to ensure a substantial plastic deformation of samples, and intense shrinkage is observed. In the second NPT the structure is perfected during plastic deformation in shrinkage and point defects (single vacancies) get transported to the surface of the crystals. The amount of single vacancies abruptly decreases and the conductivity becomes lower. This process is less related to the initial particle size, since the surface properties to a large extent are leveled in transition via the first maximum. The smaller the particles, the more perceptible is perfecting of the structure in the first nonequilibrium phase transition (the higher the maximum).

Hot injection molding is usually applied in the second bifurcation interval (elimination of the bifurcation using an external controlling signal). One decreases the rate of temperature rise in the temperature interval of intense shrinkage or implements an exposure [16] (thus providing conditions for inheriting the structure.)

The third main bifurcation (the third NPT) in producing high-density ceramics is related to the modification of the structure of an infinite cluster consisting of open pores (start of transition of some sealed pores into open pores). The evolution of the skeleton as well passes via a possible bifurcation area (the third maximum in Fig. 1), after which rapid growth of crystals is observed in ceramics.

Fast growth of crystals after reaching a certain level of porosity (approximately 10% of the total porosity) has been long known to technologists. To obtain pore-free ceramics from highly disperse powders, the growth of crystals should start after reaching a maximum possible level of relative density of the molded piece [17]. Such behavior of the system can be achieved by selecting respective doping impurities and using highly disperse powders. In the context of synergism, this means conservation of the topological structure of the infinite cluster consisting of open pores by elimination of the bifurcation using an internal signal, i.e., dopant impurities.

In firing, some processes occur in oxides on the sub-micron level, which can be comprehended using the quasichemical approach. Predominant volatilization of oxygen at high temperatures causes a protective reaction of the system in the form of a potential barrier formed at the crystal boundary due to an increased concentration of oxygen vacancies there. This barrier impedes the diffusion processes of crystal growth [4]. At the same time, a high concentration of vacancies leads to a loss of stability in the crystalline structure of material at the crystal boundaries and facilitates its plastic deformation. The height of this concentration barrier depends on the energy parameters (fractality) of this segment of the surface. The faster and more intensely oxygen anions

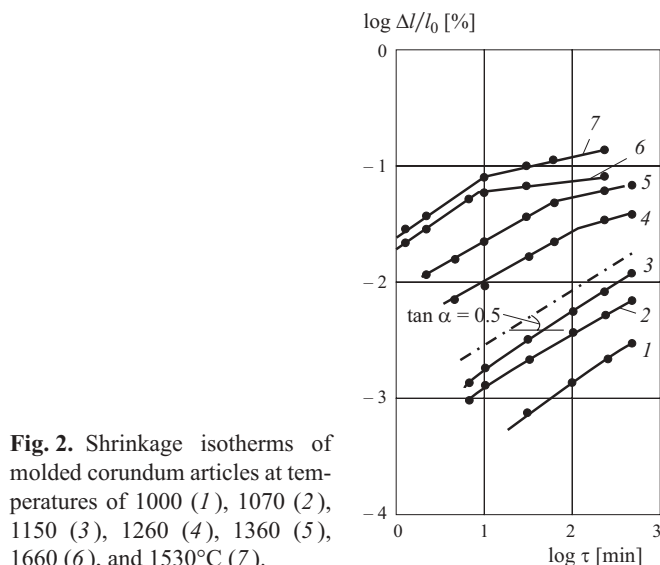


Fig. 2. Shrinkage isotherms of molded corundum articles at temperatures of 1000 (1), 1070 (2), 1150 (3), 1260 (4), 1360 (5), 1660 (6), and 1530°C (7).

volatilize from the crystal boundary, the higher is the emerging concentration barrier.

The barrier prevents further volatilization of oxygen and mass transfer via the boundary, i.e., impedes the growth of crystals. For mass transfer to take place, a coordinated motion of cations and anions is required, and the process is controlled by the motion of the slowest ions. The total electric current should be equal to zero. In vacancy diffusion, the mass transfer is controlled by the vacancies whose concentration is minimal compared to a required quantity. Cations vacancies play this role in sintering of most oxides [18].

Deformations of the crystalline structure in the near-surface layer intersected by the diffusion path accelerate the diffusion processes oriented to perfecting the structure. A high concentration of vacancies in the surface layer of a crystal, for instance, Al_2O_3 contributes to oxygen vacancies joining with cation vacancies and forming electroneutral associates, i.e., molecular pores (reactions (1)).

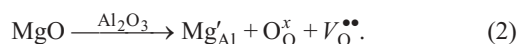
The concentration barrier for oxygen monovacancies presumably does not affect such associates. These associates overcome the concentration barrier, reach the boundary, which is the vacancy outlet, and annihilate in open pores in the course of plastic deformations in shrinkage. This process is intense, while the system of boundaries provides for removal of molecular pores to the sample surface. For this purpose, the most efficient is an infinite cluster consisting of open pores connected with the surface of the molded sample. This can account for a known fact that crystals in sintering virtually do not grow until reaching a certain minimum of total porosity (about 10%). The process of modification of the structure of the infinite open-pore cluster after some open pores transform into sealed ones corresponds to the third main unstable state.

In sintering the infinite cluster of open pores in certain segments of the article transforms into sealed pores, which are spaces insulated from the surface. The formation of such pores together with perfecting the surface crystal layers and

intercrystalline boundaries impedes predominant volatilization of oxygen from the surface layers of crystals. This decreases the concentration of nonstoichiometric oxygen vacancies in the surface layer and the oxygen diffusion rate. As a result, in recrystallization of dense ceramic it can become lower than the rate of cations [4]. The concentration barrier for oxygen monovacancies on the crystal surface decreases so much, that they start overcoming it in a required ratio to cation vacancies, thus causing mass transfer and crystal growth. Furthermore, a decrease in the shrinkage rate and, accordingly, in the intensity of plastic deformation prevents efficient use of the mechanism of annihilation of vacancies in open pores. The role of plastic deformation is confirmed by the fact that using highly disperse powders, one can often produce denser ceramics from less dense intermediate articles, in which plastic deformation in shrinkage is more intense [4].

If the degree of the process nonequilibrium is such that the system does not have time to remove all molecular pores to the sample surface, then sealed pores start acting as vacancy outlets. In that case the growth of crystals starts long before all molecular pores are removed, and it becomes impossible to obtain pore-free ceramics. The presence of pores in sintered ceramics is an example of accumulation of energy in the form of new surfaces.

To remove the third bifurcation using internal controlling signals, one uses dopant impurities impeding diffusion mass transfer. This delays the evolution of the infinite open-pore cluster into spaces separated from the surface (a system of sealed pores). In making clear corundum ceramics, dopant impurities (MgO) were used, which create oxygen vacancies and thus retards the diffusion mass transfer:



Usually, diffusion in oxides in the case of the vacancy mechanism is limited by a concentration of cation vacancies. They arise when the host lattice cations in a solid solution are replaced by impurity cations with a higher degree of oxidation. For instance, magnesium vacancies arise in dissolution of Sc_2O_3 in MgO :

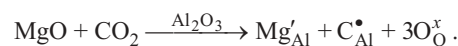


Cation vacancies arise as well in the case when an impurity cation of any degree of oxidation penetrates into an interstice. For instance, cation vacancies are formed when Li_2O dissolves in CaO .



An increase in the concentration of cation vacancies stimulates diffusion mass transfer, and its decrease (for instance due to an increased quantity of oxygen vacancies) suppresses it. Experiments revealed a negative role of carbon from alkoxy groups penetrating into the structure, which neutralized the effect of magnesium cations and decreased the concentration of oxygen vacancies, which prevented the pro-

duction of clear samples [19]. This can be attributed to the fact that carbon decreases the concentration of oxygen vacancies formed according to reaction (2):



As a consequence, diffusion mass transfer is intensified, pores become occupied with fast growing crystals, and ceramics loses clarity.

The use of easily volatilizing tungsten and molybdenum oxides as dopants in sintering dense mullite as well presumably facilitates the preservation of the infinite open-pore cluster up to reaching high density (USSR Inventor's Certif. No. 1218629). Easily volatilizing oxides prevent open pores transforming unto sealed pores.

An example of self-organization is superfast sintering, when a sample is placed into a furnace preheated to the sintering temperature. As a result of passing all three main unstable states in a high degree of nonequilibrium, it becomes possible to obtain dense fine-crystalline samples. This method is acceptable only for making small parts of simple shapes, for instance, small milling balls. It is more promising to use microwave heating, which provides for fast volume heating of the molded piece and decreases the temperature gradient.

In making high-density ceramics, technologists used to empirically eliminate main unstable states and multistabilities. Synergism opens ways for a more systematic analysis of technological processes and development of materials with preset structure and properties. Manifestations of these three main bifurcations intensify with an increasing degree of nonequilibrium of the sintering process, i.e., as the powder particle size decreases, especially in producing nanoceramics.

In producing dense ceramics, when sintering occurs simultaneously with chemical reactions of the formation of complex oxides, another possible main bifurcation is added to the three listed above, which is related to volumetric changes as a consequence of the chemical reaction, which influences the evolution of the skeleton structure and raises the degree of nonequilibrium diffusion mass transfer. Such bifurcation actually plays the role of the first main bifurcation observed in sintering without a chemical reaction, the local compactions disappear in it and new ones arise (an abrupt modification of the skeleton structure). As a consequence of self-organization, a skeleton consisting of compact sites is formed, with large pores between them that cannot be removed in the final stage of sintering and, consequently, it becomes impossible to obtain high-density ceramics. This can be interpreted as accumulation of a part of energy in the system for the formation of new surfaces (pores).

To remove this bifurcation, dopant impurities of scandium and yttrium oxides and rare-earth element oxides were used as internal controlling signals in sintering of mullite ceramics based on a mixture of single oxides. The prevalent sorption of dopant impurities on aerosil (SiO_2) and formation of oxygen vacancies made it possible to retard the diffu-

sion flow of silicon cations and to make it less intense than the flow of aluminum cations. In these conditions all bifurcation were presumably eliminated and it became possible to ensure the evolution of the structure to high-density ceramics.

Another method for elimination of multistability in chemical reactions is to use a mixture of two preliminary synthesized compositions, one of which is close to a eutectic composition and the second one is close to the compound synthesized. The total composition of the mixture corresponded to the desired chemical compound (USSR Inventor's Certif. No. 1071607). This decreased the degree of the process nonequilibrium during the chemical reaction. Particular compositions were selected, which ensured elimination of multistability and evolution of the structure toward dense ceramics.

The synergistic approach makes it possible to reveal general regularities of the process at various stages of ceramic technology. This facilitates understanding and opens possibilities for extrapolating these regularities from some processes to others.

Within the synergistic concept it is possible to propose an algorithm for the development of new ceramic technologies based on identification of intervals of the main unstable states for a system and either using them for self-organization, or eliminating them by means of internal or external controlling signals.

The quasichemical approach makes it possible to determine, which defects may prevent or facilitate diffusion mass transfer in ceramics, in particular, sintering. Implementation of these processes to a large extent depends on the degree of process nonequilibrium determined by technological factors: the prehistory of powder (its purity, dispersion, and degree of aggregation), the conditions of molding the intermediate piece, its density and uniformity of density, the conditions of TTb removal and the composition of the TTb, the sintering regime, the composition and pressure of the gaseous medium. One should not attribute too great significance to reactions of defect formation, since one cannot always be sure that a reaction actually occurs as it is written. However, the quasichemical approach makes it possible to give a qualitative interpretation of numerous phenomena in ceramic technology: the principles of selecting additives for acceleration or deceleration of diffusion mass transfer, for stabilization of desirable polymorphous modifications, selection of a gaseous medium for firing, etc. It opens ways to estimating a concentration of point defects in crystals, and, consequently to selecting the type and quantity of additives, the partial pressure of the gas medium for firing, the temperature of preliminary thermal treatment of powder, and the temperature regimes for ceramics sintering.

A theoretical substantiation and identification of the regularities of a prehistory affecting modifications of article structure is a topical problem, whose solution will open way for a substantial improvement of service properties and ensure a steady quality. This makes it possible to generalize accumulated extensive experimental data, to get deeper under-

standing of the essence of technological processes and the role of internal (prehistory, structure inheriting) and external (conditions of the process) controlling factors in formation of a desired structure, and to trace ways for improving the quality of materials and articles produced.

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